WRI-08-R016R

FINAL REPORT

Base Program on Energy Related Research

Reporting Period: April 1998 – April 2008

Under Cooperative Agreement
DE-FC26-98FT40322

For
U.S. Department of Energy
Office of Fossil Energy
National Energy Technology Laboratory
Morgantown, West Virginia

By
Western Research Institute
Laramie, Wyoming

DISCLAIMER

EXECUTIVE SUMMARY

From April 1998 through April 2008, Western Research Institute (WRI) performed energy and related environmental research under a ten-year Cooperative Agreements, DE-FC26-98FT40322, Base Research Program. Over the course of the Program, a total of fifty nine tasks were proposed, see table below. This report summarizes the results from the Program.

COOPERATIVE AGREEMENT NO. DE-FC26-98FT40322 -- BASE PROGRAM

Task No.	Title	Total Expended
1.1	CROW Process Application for Sites Contaminated with LNAPL and Chlorinated Solvents	474,995.85
1.2	Petroleum Residua Solubility Parameter/Polarity Map	77,160.11
1.3	Laboratory and Bench-Scale Testing for Treating Used Motor Oil	214,108.49
1.4	Coal-Fired Gas Turbine	0.00
1.5	Combustion and Conversion Technologies for Western US Coals	1,054,317.00
1.6	Deposition from Heavy Oils	184,819.94
1.7	Development of a Stimulation Method for Coalbed Methane Wells	332,985.69
1.8	Residua Upgrading Efficiency Improvements Models: Coke Formation Predictability Maps	722,154.71
1.9	Technical Assistance Program for Energy Operators	188,000.00
1.a	Development of an In-Situ Method for Measuring Sorbed Methane in Coal Beds	50,000.00
1.b	Biomass to Hydrogen via Bromine Processing	28,609.25
1.c	Using a Plasma Stream to Stabilize Unsaturated Oil Fractions	44,812.98
1.d	Direct Catalytic Liquefaction of Coal	77,380.39
1.e	Removal of Mercury from Coal-Derived Synthesis Gas	30,000.00
1.f	Catalytic Synthesis Applications for Ionic Liquids	325,000.00
1.g	Enhanced Petroleum Productions Using Horizontal Wells	13,754.00
1.h	Heavy Oil Processing	287,000.00
1.i	Disposition of Mercury in Sequestration Ready Power Systems	130,000.00
1.j	Advanced Processing of Coal	411,728.00
1.k	Assessment of Oil Shale Development Issues and Opportunities	0.00
1.l	Participation with the NCUT in the "Upgrading and Refining of Heavy Oil, Bitumen and Synthetic Crude Oil" Conference	30,000.00
2.1	Development of a Versatile New Technology for the Cleanup of Metals Contaminated Waters	107,580.34
2.2	PEACTM Protective Covering	15,000.00
2.3	Dry Flue Gas Desulphurization Ash-Based Construction Materials-Environmental and Geotechnical Performance	145,372.00
2.4	Pre-Combustion Thermal Removal of Hazardous Air Pollutants (HAPs) from Coal	345,415.00
2.5	Controlling Redox Potential to Reduce or Eliminate the Formation of Acid in Acid Mine Drainage and Reclamation Problems	231,716.43
2.6	Remediation of MTBE Contaminated Aquifers and Soils	267,023.08
2.7	Evaluating the Use of Produced Water Generated During Coalbed Methane Extraction for Land Application in the Powder River Basin -- Field Project	224,602.00
2.8	Alternative CO2 Sequestration Media-Integration with Phosphogypsum Resources	1,823.00
2.9	Improved Catalysts for Alcohol Synthesis	850,530.00
2.a	Barium Removal from Coalbed Methane-Produced Water	118,565.64
2.b	Upstream Control of an Oil Field Production Facilities Pollution Source	119,061.00
2.c	Use of Polymers in the Ash Management and the Construction Industry	4,296.00
2.d	Application of Uric Acid/Farm Wastes as a Slow-Releasing Nitrogen Source for Enhanced Bioremediation of Petroleum Contaminated Soils and Groundwate	165,000.00
2.e	Applications of Layered Double Oxides in Removing Oxyanions from Oil Refining and Coal Mining Wastewater	120,064.08
2.f	Enhancement of Biogenic CBM Production and Back Injection of CBM Produced Water	75,000.00
2.g	Ash Management Options for Emerging Countries	14,000.00
2.h	Potential Mercury Problems in Oil Shales	40,000.00
2.i	Synergistic Combination of Petroleum Hydrocarbon Biodegradation and Microbial Fuel Cell	240,000.00
2.j	Extraction of Bio-Surfactant from Thermophiles for Petroleum Applications -- Phase I	45,000.00
2.k	Sorbent Test Facility for Power Plant Emissions Control	65,000.00
3.1	Heavy Oil/Plastics Co-Processing	143,090.87
3.2	Pilot-Scale Testing of WRI's Plastics Recycling Technology	121,910.00
3.3	Development of a Feed System for Stand-Alone Pyrolyzer	140,449.65
3.4	Alternate Approaches to Olefin Reduction in Pyrolysis Products	84,438.59
3.5	Development of an On-Line Alkali Monitor	138,362.92
3.6	A New Product from Used Motor Oil and Waste Plastics	60,000.00
3.7	Evaluation of Producing Building Materials with Coal Combustion Products and Biomass	44,370.00
3.8	Field Screening for Halogenated Volatile Organic Compounds	320,066.00
3.9	Enhanced Processing Options for Biomass Fractionations	184,553.00
3.a	Production of Syngas from Methane Using Membrane Reactors	85,000.00
3.b	Optimization of the TaBoRR Stripper	465,000.00
3.c	Ultrasonic Spectroscopy	10,005.72
3.d	Phase Change Liquids	86,000.00
3.e	Technical Assistance to the Subbituminous Coal Producers and Users	302,434.36
3.f	Development of Small-Scale Vapor Recovery Units	35,024.00
3.g	Biomass Pretreatment Approach for Recovery of Lignin and Sugars	565,475.00
3.h	Potential Product Stabilization Options for WRI's Thermal Pre-Combustion Mercury Removal Process	177,046.00
4.0	Program and Management Support	298,898.91
	Total	**11,134,000.00**

The main objective of the Base Research Program was to conduct both fundamental and applied research that will assist industry in developing, deploying, and commercializing efficient, nonpolluting fossil energy technologies that can compete effectively in meeting the energy requirements of the Nation. In that regard, tasks proposed under the WRI research areas were aligned with DOE objectives of secure and reliable energy; clean power generation; development of hydrogen resources; energy efficiency and development of innovative fuels from low and no-cost sources.

The goal of the Base Research Program was to develop innovative technology solutions that will:

- Increase the production of United States energy resources – coal, natural gas, oil, and renewable energy resources;
- Enhance the competitiveness of United States energy technologies in international markets and assist in technology transfer;
- Reduce the nation's dependence on foreign energy supplies and strengthen both the United States and regional economies; and
- Minimize environmental impacts of energy production and utilization.

This report summarizes the accomplishments of the overall Base Program. This document represents a stand-alone Final Report for the entire Program. It should be noted that an interim report describing the Program achievements was prepared in 2003 covering the progress made under various tasks completed during the first five years of this Program.

Progress on the tasks is grouped in technology/focus areas, as follows:

- CROW Process Development
- Heavy Oil Processing and Petroleum Refining Efficiency Improvements
- Development and Testing of TaBoRR/WRITE Technologies
- Combustion and Conversion Technologies for Western U.S. Coals
- Technical Assistance and Technology Transfer Programs
- Oil and Gas Production
- Catalysis and Synthesis/Liquid Fuels
- Coal Bed Methane Produced Waters
- Beneficial Uses of Coal Combustion Products
- Biomass Processing
- HAPs Emissions and Mitigation
- VOC Sampling and Sample Storage
- Advanced Remediation Technologies

WRI Base Program supported the development of energy and environment-related technologies consistent with DOE priorities. Individual tasks addressed the needs of coal, oil and gas, and biomass-based energy systems.

Under the Cooperative Agreement, WRI has built a modular, well-instrumented coal combustion test facility that mimics a coal-fired utility boiler in residence time and furnace temperature profile. This facility is being used for technology development and technology verification projects for national and international utilities, for coal technology companies, and for combustion and emissions control equipment manufacturers.

- working with our clients, we are testing new and cheaper methods for reducing NOx emissions such as injection of coal and biomass-based slurries, injection of hydrogen and syngas, injection of ozone;
- working with our clients, we are testing cheaper sorbents and methods for capturing mercury. One such scheme reinjects the unburnt carbon recovered from the fireball of the boiler to capture mercury. This technology, thief carbon, can reduce the cost of mercury capture to a fraction of that for conventional activated carbon. Thanks to our cooperative agreement with the USDOE, the thief carbon WRI made in the CTF was recently injected by a utility in a 600MW unit to show that indeed thief carbon is nearly as effective as activated carbon;
- working with our clients we are testing advanced combustion concepts such as oxy-fuel combustion as a multi-pollutant control strategy for not only the sequestration-ready, power plants of the future but developing a technology that can benefit our existing fleet of power plants; and
- working with our clients, we are looking to the future and testing cheaper ways of making oxygen. Novel concepts for separating oxygen from air for use in the coal combustion processes are being tested at the combustion test facility.

WRI has been developing synthesis technologies to produce transportation fuels. One such technology can convert any carbonaceous feedstock into a mixture of alcohols, and the mixture is ready for use as a gasoline blend.

- Imagine a confined animal feedlot. Animal waste is collected and processed in bio-digesters. Using the technology being demonstrated by WRI and partners, the digester gas becomes a mixture of alcohols for use in our cars, a transportation fuel.
- Imagine a remote abandoned natural gas field. Using the technology being demonstrated, this field can make transportation fuel that can be trucked to the markets.
- Imagine a biorefinery where forestry waste, animal waste, agricultural waste is processed using the technology developed at WRI to convert these renewable feedstock into transportation fuel.
- Imagine a power plant where Wyoming coal is the feed. Using the technology developed at WRI under the Cooperative Agreement, the plant not only produces electricity but also synthesizes a mixture of alcohols.

In conjunction with the appropriate gasification scheme this synthesis technology is a coal-to-liquids technology. In the same spirit, for remote natural gas fields this technology is a gas-to-liquid technology. As a biogas-based system, this technology is a means of capturing and converting green house gasses into a useful product.

Under the auspices of the Cooperative agreement, WRI is developing and testing unique, low-cost biomass gasification technologies for smaller-scale, distributed power generation applications. At WRI, we believe that our Nation's farmers and renewable energy are an essential part of our energy future. Technologies for distributed power generation and distributed production of synthetic fuels and chemicals from renewable resources have been an integral part of research under the Cooperative Agreement.

Under the auspices of the Cooperative Agreement, WRI has developed and patented a process for upgrading PRB coal by thermally removing mercury prior to combustion at the power plant, thus eliminating the need for costly carbon injection to meet new mercury regulations. A recent economic study for the Electric Power Research Institute has shown this process to be one of the lowest-cost technologies for removing mercury from PRB coal-fired power plants.

Under the auspices of the Cooperative agreement, WRI has developed a patented Thermal Enhancement (WRITE) process for heavy oil upgrading. The process a variant of the TaBoRR technology developed under the Base Program, converts bitumen (e.g. heavy oil, oil sands) into residuum-free oil whose density and viscosity meet pipeline specifications. A Canadian company has acquired the rights to the WRITE technology and is cosponsoring the development of a commercial-scale demonstration plant. When deployed, the technology will reduce our dependence on oil shipments from unstable parts of the world.

In Wyoming, CBM produced water-related environmental issues are paramount in developing this resource. Under the Cooperative Agreement, WRI worked with producers to demonstrate beneficial agricultural and related uses for this precious water. At the same time, under the Base Program several new concepts were tested for water purification and reuse.

WRI has taken a lead role in policy support for air quality regulations by creating and facilitating the Subbituminous Energy Coalition (SEC). The organization's approximately 50 members represent the major coal companies in the Powder River Basin, utilities burning PRB coal, railroads serving the PRB, and other interested parties. The SEC provides a forum for industry discussions on environmental control issues and provides a collective voice for PRB coal producers and users. The SEC has orchestrated a detailed review of proposed EPA mercury rules to ensure that subbituminous coal remains an environmentally acceptable and competitive fuel source. Looking to the future, SEC is poised to tackle CO_2 emissions and related issues.

Under the Cooperative Agreement, WRI has developed value-added uses for power plant coal combustion by-products. Use of these materials for applications such as mine-site subsidence control, soil amendment, acid mine drainage mitigation, and construction were developed and tested.

Environmental consequences of energy and fuels production are paramount in our research programs. Under the auspices of the Cooperative Agreement, WRI scientists are developing and testing site-specific bio-remediation technologies for restoring contaminated soils and water.

WRI has developed or made significant contributions to several environmental testing and sampling instruments currently (or soon to be) commercially available. Examples include Soil Test Kit for in-the-field quantitative analysis of hydrocarbon contaminants in soil, integrated storing field soil samples for volatile analysis, and the X-Wand, an instrument for measuring halogenated volatile organic compounds, a common but difficult to measure class of contaminants. All three are commercially available.

Looking to the future, WRI is continuing to implement an ambitious research and technology demonstration agenda under the new five-year Cooperative Agreement. With the establishment of the state-supported University of Wyoming School of Energy Resources, there is an opportunity for collaborative research between the University faculty and WRI staff. Collaborative research will also allow us to add an education and training component to our Cooperative Agreement projects thereby meeting our demand for trained energy professionals.

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BACKGROUND

From April 1998 through April 2008, Western Research Institute (WRI) performed energy and related environmental research under a ten-year Cooperative Agreements, DE-FC26-98FT40322, Base Research Program. The Base Research Program at WRI was planned to develop technologies and concepts to a level that will attract industrial sponsors for continued development under the Jointly Sponsored Research (JSR) Program and eventual commercialization. Both peer and management reviews were employed prior to proposing Base projects to the U.S. Department of Energy (DOE).

Over the ten year period of performance of the Cooperative Agreement, fifty eight individual tasks were proposed in three broad technology areas viz., Energy Program (21 tasks), Environmental Program (20 tasks), and Technology Enhancement Program (17 tasks).

The Base Cooperative Agreement (DE-FC26-98FT40322) was initiated on April 10, 1998, with funding of $500,000 for the first year. Since that time WRI has maintained a 1/3 to 2/3 relationship in Base and JSR funding. Exact funding levels and the number of projects for each of the ten funding years under this Cooperative Agreement is shown in Table 1 below. Funding for individual tasks as approved is displayed in Table 2. Over the course of Program, with DOE concurrence, WRI redeployed some of the funds among different tasks. Those changes in funding are reflected in a column labeled "Total Expended".

Table 1. Summary of Base Funding Over the Course of the Cooperative Agreement

Fiscal Year	Funding	Number of Projects	New Starts
1998	$500,000	7	7
1999	$1,045,000	13	6
2000	$1,326,500	20	7
2001	$1,303,000	25	5
2002	$1,330,000	31	6
2003	$1,323,000	38	7
2004	$1,330,000	46	8
2005	$1,300,000	51	5
2006	$950,000	57	6
2007	$712,500	58	1

Table 2. COOPERATIVE AGREEMENT NO. DE-FC26-98FT40322 -- BASE PROGRAM

Task No.	Title	AS PROPOSED										Total Approved	Total Expended
		BP1	BP2	BP3	BP4	BP5	BP6	BP7	BP8	BP9	BP10		
1.1	CROW Process Application for Sites Contaminated with LNAPL and Chlorinated Solvents	50,000	114,886	199,943	110,000	0	0	0	0	0	0	474,829.00	474,995.85
1.2	Petroleum Residua Solubility Parameter/Polarity Map	75,000	0	0	0	0	0	0	0	0	0	75,000.00	77,160.11
1.3	Laboratory and Bench-Scale Testing for Treating Used Motor Oil	135,000	0	0	0	0	0	0	0	0	0	135,000.00	214,108.49
1.4	Coal-Fired Gas Turbine	140,000	0	0	0	0	0	0	0	0	0	140,000.00	0.00
1.5	Combustion and Conversion Technologies for Western US Coals	0	174,627	220,326	150,024	199,000	150,000	150,000	0	0	0	1,043,977.00	1,054,317.00
1.6	Deposition from Heavy Oils	0	183,818	0	0	0	0	0	0	0	0	183,818.00	184,819.94
1.7	Development of a Stimulation Method for Coalbed Methane Wells	0	0	122,903	100,000	125,000	0	0	0	0	0	347,903.00	332,985.69
1.8	Residua Upgrading Efficiency Improvements Models: Coke Formation Predictability Maps	0	0	197,046	125,057	150,000	100,000	150,000	0	0	0	722,103.00	722,154.71
1.9	Technical Assistance Program for Energy Operators	0	0	0	0	98,000	90,000	0	0	0	0	188,000.00	188,000.00
1.a	Development of an In-Situ Method for Measuring Sorbed Methane in Coal Beds	0	0	0	0	50,000	0	0	0	0	0	50,000.00	50,000.00
1.b	Biomass to Hydrogen via Bromine Processing	0	0	0	0	0	25,000	0	0	0	0	25,000.00	28,609.25
1.c	Using a Plasma Stream to Stabilize Unsaturated Oil Fractions	0	0	0	0	0	50,000	0	0	0	0	50,000.00	44,812.98
1.d	Direct Catalytic Liquefaction of Coal	0	0	0	0	0	75,000	0	0	0	0	75,000.00	77,380.39
1.e	Removal of Mercury from Coal-Derived Synthesis Gas	0	0	0	0	0	0	30,000	0	0	0	30,000.00	30,000.00
1.f	Catalytic Synthesis Applications for Ionic Liquids	0	0	0	0	0	0	75,000	150,000	100,000	0	325,000.00	325,000.00
1.g	Enhanced Petroleum Productions Using Horizontal Wells	0	0	0	0	0	0	25,000	0	0	0	25,000.00	13,754.00
1.h	Heavy Oil Processing	0	0	0	0	0	0	0	125,000	100,000	62,000	287,000.00	287,000.00
1.i	Disposition of Mercury in Sequestration Ready Power Systems	0	0	0	0	0	0	0	130,000	0	0	130,000.00	130,000.00
1.j	Advanced Processing of Coal	0	0	0	0	0	0	0	120,000	130,000	140,000	390,000.00	411,728.00
1.k	Assessment of Oil Shale Development Issues and Opportunities	0	0	0	0	0	0	0	0	30,000	0	30,000.00	0.00
1.l	Participation with the NCUT in the "Upgrading and Refining of Heavy Oil, Bitumen and Synthetic Crude Oil" Conference	0	0	0	0	0	0	0	0	30,000	0	30,000.00	30,000.00
2.1	Development of a Versatile New Technology for the Cleanup of Metals Contaminated Waters	15,000	90,064	0	0	0	0	0	0	0	0	105,064.00	107,580.34
2.2	PEACTM Protective Covering	15,000	0	0	0	0	0	0	0	0	0	15,000.00	15,000.00
2.3	Dry Flue Gas Desulphurization Ash-Based Construction Materials-Environmental and Geotechnical Performance	0	0	149,980	0	0	0	0	0	0	0	149,980.00	145,372.00
2.4	Pre-Combustion Thermal Removal of Hazardous Air Pollutants (HAPs) from Coal	0	0	194,627	153,025	0	0	0	0	0	0	347,652.00	345,415.00
2.5	Controlling Redox Potential to Reduce or Eliminate the Formation of Acid in Acid Mine Drainage and Reclamation Problems	0	0	106,675	0	125,000	0	0	0	0	0	231,675.00	231,716.43
2.6	Remediation of MTBE Contaminated Aquifers and Soils	0	0	0	207,000	60,000	0	0	0	0	0	267,000.00	267,023.08
2.7	Evaluating the Use of Produced Water Generated During Coalbed Methane Extraction for Land Application in the Powder River Basin -- Field Project	0	0	0	132,141	0	0	0	0	0	0	132,141.00	224,602.00
2.8	Alternative CO2 Sequestration Media-Integration with Phosphogypsum Resources	0	0	0	95,018	0	0	0	0	0	0	95,018.00	1,823.00
2.9	Improved Catalysts for Alcohol Synthesis	0	0	0	135,030	0	120,000	125,000	190,000	130,000	150,500	850,530.00	850,530.00
2.a	Barium Removal from Coalbed Methane-Produced Water	0	0	0	0	60,000	60,000	0	0	0	0	120,000.00	118,565.64
2.b	Upstream Control of an Oil Field Production Facilities Pollution Source	0	0	0	0	0	120,000	0	0	0	0	120,000.00	119,061.00
2.c	Use of Polymers in the Ash Management and the Construction Industry	0	0	0	0	0	0	26,000	25,000	0	0	51,000.00	4,296.00
2.d	Application of Uric Acid/Farm Wastes as a Slow-Releasing Nitrogen Source for Enhanced Bioremediation of Petroleum Contaminated Soils and Groundwate	0	0	0	0	0	0	90,000	75,000	0	0	165,000.00	165,000.00
2.e	Applications of Layered Double Oxides in Removing Oxyanions from Oil Refining and Coal Mining Wastewater	0	0	0	0	0	0	75,000	15,000	0	30,000	120,000.00	120,064.08
2.f	Enhancement of Biogenic CBM Production and Back Injection of CBM Produced Water	0	0	0	0	0	0	0	75,000	0	0	75,000.00	75,000.00
2.g	Ash Management Options for Emerging Countries	0	0	0	0	0	0	0	0	35,000	0	35,000.00	14,000.00
2.h	Potential Mercury Problems in Oil Shales	0	0	0	0	0	0	0	0	40,000	0	40,000.00	40,000.00
2.i	Synergistic Combination of Petroleum Hydrocarbon Biodegradation and Microbial Fuel Cell	0	0	0	0	0	0	0	0	140,000	140,000	280,000.00	240,000.00
2.j	Extraction of Bio-Surfactant from Thermophiles for Petroleum Applications -- Phase I	0	0	0	0	0	0	0	0	45,000	0	45,000.00	45,000.00
2.k	Sorbent Test Facility for Power Plant Emissions Control	0	0	0	0	0	0	0	0	0	65,000	65,000.00	65,000.00
3.1	Heavy Oil/Plastics Co-Processing	70,000	0	0	0	0	0	0	0	0	0	70,000.00	143,090.87
3.2	Pilot-Scale Testing of WRI's Plastics Recycling Technology	0	136,945	0	0	0	0	0	0	0	0	136,945.00	121,910.00
3.3	Development of a Feed System for Stand-Alone Pyrolyzer	0	124,077	0	0	0	0	0	0	0	0	124,077.00	140,449.65
3.4	Alternate Approaches to Olefin Reduction in Pyrolysis Products	0	82,719	0	0	0	0	0	0	0	0	82,719.00	84,438.59
3.5	Development of an On-Line Alkali Monitor	0	137,864	0	0	0	0	0	0	0	0	137,864.00	138,362.92
3.6	A New Product from Used Motor Oil and Waste Plastics	0	0	60,000	0	0	0	0	0	0	0	60,000.00	60,000.00
3.7	Evaluation of Producing Building Materials with Coal Combustion Products and Biomass	0	0	50,000	0	0	0	0	0	0	0	50,000.00	44,370.00
3.8	Field Screening for Halogenated Volatile Organic Compounds	0	0	0	70,066	75,000	75,000	100,000	0	0	0	320,066.00	320,066.00
3.9	Enhanced Processing Options for Biomass Fractionations	0	0	0	0	90,000	90,000	0	0	0	0	180,000.00	184,553.00
3.a	Production of Syngas from Methane Using Membrane Reactors	0	0	0	0	50,000	35,000	0	0	0	0	85,000.00	85,000.00
3.b	Optimization of the TaBoRR Stripper	0	0	0	0	215,000	200,000	0	50,000	0	0	465,000.00	465,000.00
3.c	Ultrasonic Spectroscopy	0	0	0	0	0	10,000	0	0	0	0	10,000.00	10,005.72
3.d	Phase Change Liquids	0	0	0	0	0	27,000	24,000	0	0	35,000	86,000.00	86,000.00
3.e	Technical Assistance to the Subbituminous Coal Producers and Users	0	0	0	0	0	50,000	75,000	65,000	50,000	60,000	300,000.00	302,434.36
3.f	Development of Small-Scale Vapor Recovery Units	0	0	0	0	0	0	80,000	0	0	0	80,000.00	35,024.00
3.g	Biomass Pretreatment Approach for Recovery of Lignin and Sugars	0	0	0	0	0	0	250,000	175,000	60,000	0	485,000.00	565,475.00
3.h	Potential Product Stabilization Options for WRI's Thermal Pre-Combustion Mercury Removal Process	0	0	0	0	0	0	0	50,000	35,000	0	85,000.00	177,046.00
4.0	Program and Management Support	0	0	25,000	25,639	33,000	46,000	55,000	55,000	39,000	30,000	308,639.00	298,898.91
	Total	**500,000**	**1,045,000**	**1,326,500**	**1,303,000**	**1,330,000**	**1,323,000**	**1,330,000**	**1,300,000**	**964,000**	**712,500**	**11,134,000.00**	**11,134,000.00**

The main objective of the Base Research Program was to conduct both fundamental and applied research that will assist industry in developing, deploying, and commercializing efficient, nonpolluting fossil energy technologies that can compete effectively in meeting the energy requirements of the Nation. WRI is located in Wyoming, the Btu capitol of the United States. Our proximity to the energy resources in the Western United States gives us a heightened sense of responsibility and purpose in how we conduct business and set direction for our research projects. In that regard, tasks proposed under the WRI research areas were aligned with DOE objectives of secure and reliable energy; clean power generation; development of hydrogen resources; energy efficiency and development of innovative fuels from low and no-cost sources.

The goal of the Base Research Program was to develop and commercialize technologies that will:

- Increase the production of United States energy resources – coal, natural gas, oil, and renewable energy resources;
- Enhance the competitiveness of United States energy technologies in international markets and assist in technology transfer;
- Reduce the nation's dependence on foreign energy supplies and strengthen both the United States and regional economies; and
- Minimize environmental impacts of energy production and utilization.

The Program was based on industrial/governmental partnerships and focused research in three major technology areas:

- ENERGY PROGRAM, which emphasized energy independence through increased production and use of domestic energy resources including enhanced oil recovery; heavy oil upgrading; recovery of value-added products from abandoned gas fields; development of gas-to-liquid technologies; coal beneficiation, upgrading and use; enhanced coalbed methane recovery; development of technologies for the production of hydrogen and other alternate fuels from fossil fuels; and the development of renewable energy resources.
- ENVIRONMENTAL PROGRAM, which minimized the impact of energy production and use of U.S. and sub-bituminous western coals, oil and gas, and coalbed methane resources. Efforts focused on technologies and technical services for mitigation of HAPs (Hazardous Air Pollutants) emissions such as mercury from coal-fired power plants, use of coal combustion by-products in novel applications, mitigation of the impact of produced waters from coalbed methane development, re-vegetation of abandoned mine lands through the development of synthetic soils, bioremediation of oil-contaminated materials, and use of waste biomass in bio-refinery applications.

- TECHNOLOGY ENHANCEMENT PROGRAM activities included those that help mitigate the environmental effects of energy production and/or lead to more efficient energy production from strategic resources, including the development and improvement of environmental sensors, resource models, and process controls.

This report summarizes the accomplishments of the overall Base Program. This document represents a stand-alone Final Report for the entire Program. It should be noted that an interim report describing the Program achievements was prepared in 2003 covering the progress made under various tasks completed during the first five years of this Program.

In order to portray a cohesive picture of the work performed under this Program, in this report we have combined the discussion of various tasks. Often multiple individual tasks proposed under this Program supported a single technology, such as CROW, TaBoRR, WRITE, Heavy Oil Upgrading, and Coal Utilization and Conversion Technologies and related Facilities Development. In such cases, for the sake of completeness, if warranted some of the work reported earlier is included in this report also.

RESEARCH HIGHLIGHTS

CROW Process Development
Tasks 1.1 and 2.6

Under previous Cooperative Agreements, WRI developed an in-situ remediation technology, Contained Recovery of Oily Wastes, CROW™. The patented process is an in-situ thermal flushing process that reduces concentrations of oily wastes in subsurface soils, aquifers, and underlying bedrock to residual saturations, thereby immobilizing them.

CROW Facilities at Bell Lumber and Pole

Because it uses steam and hot water to extract contaminants, such as coal tar, creosote, and petroleum products, directly from the ground, the CROW™ process eliminates the need for excavation, minimizing disturbance to the site and reducing costs. Further economy is achieved when recovered organic stock is reused or sold. The technology has been successfully applied at two former manufactured gas plants (MGPs), and a large wood treatment site. These three CROW process applications all occurred at sites contaminated with coal tars or fuel oil and pentachlorophenol (PCP) mixtures, contaminants generally denser than water, classified as dense non-aqueous phase liquids (DNAPLs). While DNAPL-contaminated sites are abundant, there are also many sites contaminated with gasoline, diesel fuel, or fuel oil, which are lighter than

water and lie on top of an aquifer, classified as light non-aqueous phase liquids (LNAPLs). A third type of contaminants is chlorinated hydrocarbons. These contaminants tend to accumulate very rapidly at the bottom of an aquifer.

The objective of the tasks proposed under this Cooperative Agreement was to demonstrate the effectiveness of applying the CROW process to sites contaminated with LNAPLs and chlorinated hydrocarbons (Task 1.1) and for MTBE contaminated sites (Task 2.6). Individual objectives were to determine a range of operating conditions necessary to optimize hydrocarbon recovery and/or remediation potential, to conduct numerical simulations to match the laboratory experiments and determine field-scale recoveries. For LNAPL contamination, an additional objective was to determine if chemical additions such as surfactants will increase the process efficiency.

Operating procedures were developed and tested to simulate remediation of chlorinated hydrocarbon contamination and LNAPL remediation with and without chemical addition. The results showed:

- Temperature was the most important factor in re-mediating LNAPL and chlorinated hydrocarbon contamination. Other parameters such as porosity, permeability, and water injection velocity did not appear to be as important.
- Trichloroethylene (TCE) and perchloroethylene (PCE) tests suggest that poor recoveries will be achieved unless flushing temperatures are near or above steam temperature. Removal of TCE and PCE was greater than 99% for tests with steam injection.
- Tests with three LNAPLs, diesel, wood treatment waste, and fuel oil-diesel blend all showed significant reduction in organic saturation with increasing flushing temperature. At steam temperature, diesel removal exceeded 90%. The fuel oil-diesel blend, a viscous LNAPL, required higher temperatures to have any significant removal.
- Gravity and specific gravity differences between water and the LNAPL or chlorinated hydrocarbon play an important role in their remediation. As expected, the heavier chlorinated hydrocarbons responded better to lateral flushing whereas the light LNAPL had better vertical response. As the specific gravity of the LNAPL approached the specific gravity of water, the difference between vertical and lateral response decreased.
- Chemical additives enhanced the removal of viscous LNAPLs. Removal rates were three to four times greater with surfactants than without.

For MTBE contamination, temperature was the dominant variable and the laboratory data established that even after 30 pore volumes of elevated temperature flush, sufficient MTBE and soluble gasoline components existed to produce a noticeable plume. Among the produced water treatment systems reviewed, the use of Granular Activated Carbons appeared to be the most reliable and cost effective technique.

Heavy Oil Processing and Petroleum Refining Efficiency Improvements
Tasks 1.2, 1.6, 1.8, 3.C and 1.H

Under a series of tasks, the development of a predictive model for petroleum residua coke formation was proposed with the expressed intent that rapid laboratory diagnostic analyses or on-line analytical concepts will lead to refining efficiency improvements.

Under the tasks carried out in this area, WRI developed two Coking Indexes as a diagnostic method of how near a residuum is to coke formation when heated to pyrolysis temperatures. This allows refiners to optimize cracking and distillate yields, resulting in overall improved energy efficiency in the refining processes. The indexes act as a predictor as when to stop heating a residuum to prevent fouling of heat exchangers and pipes due to coke formation. The Coking Indexes as determined from flocculation titrations or the cyclohexane-soluble portions of asphaltenes were found to apply universally to every residua material evaluated, for materials with distillate removed, and for whole visbroken oils.


Automated Flocculation Titrimeter

Research concluded under these tasks generated additional insight into a common problem in the petroleum industry related to the fouling of pipes, heat exchangers, and pumping systems in both upstream and downstream operations when heavy oils are heated or blended. The research resulted in the development of new technologies (WRI Coking Indexes US Patent 6,773,921, Automated Flocculation Titrimeter, ASTM D 6703). The AFT technology was licensed to Koehler Instruments for manufacture and sales in November 2003.

In an AFT (shown here) samples of asphalt or heavy oil, or residuum are dissolved in toluene at various concentrations and titrated with iso-octane or n-heptane at controlled temperatures to determine the point of flocculation (asphaltene precipitation) and calculate the Heithaus compatibility parameters. These results are intended primarily as a laboratory diagnostic tool for estimating the colloidal stability or compatibility of asphalt, asphalt cross blends, aged asphalt, pyrolyzed asphalt and crudes, and heavy oil, or residuum. Compatibility influences important physical properties of these materials as well as the formation of coke which causes fouling in refining processes.

The AFT is a highly automated, computerized instrument that acquires oil stability and compatibility parameters directly. The AFT can be used to perform ASTM D 6703 test method for Automated Heithaus Titrimetry. The AFT operates as a closed system with accurately controlled temperatures between 20-100°C, important for properly determining Heithaus compatibility parameters. The flocculation point is determined spectroscopically and the results are analyzed by the data acquisition system, virtually eliminating operator error in the interpretation of endpoints. The automated method is fast, accurate and very reproducible. The utility of the original Heithaus method has been expanded by developing multiple titration schemes. The software uses the data from the expanded method to predict the proximity to coke formation during heavy oil distillation. Many refiners stop distillation short of coke formation to avoid fouling in distillation equipment, tanks and transfer lines. The expanded AFT methodology allows the refiner to recover additional distillate without the fear of fouling.

The continuing effort in this area has recently lead to the development of a new separation technique and new characterization methods for upstream oil recovery improvement and downstream process monitoring for refinery efficiency improvement. A better, more rapid method to measure asphaltene solubility uses a novel on-column asphaltene precipitation and re-dissolution technique. The separations are performed using a column packed with ground polytetrafluoroethylene (PTFE). Although high performance liquid chromatography (HPLC) equipment is used, the separation does not involve adsorption or chromatographic mechanism. It is strictly solubility based.

Development and Testing of TaBoRR/WRITE Technologies
Tasks 1.3, 3.1, 3.2, 3.3, 3.4, 3.6, and 3.B

WRI developed and patented TaBoRR® (Tank Bottoms Recovery and Remediation) technology for the remediation of tank bottom wastes while recovering salable oil. The concept involved three distinct steps, 1) flash to remove water, 2) strip to recover salable oil, and 3) pyrolysis to render solids and heavy hydrocarbons to a benign, land-fillable state. Flash involves heating the tank bottoms under pressure to a temperature commensurate with the desired water removal, followed by a sudden release of pressure. As soon as the pressure is released, water and some light hydrocarbons are vaporized and sent to the flare. The flash bottoms contain hydrocarbons and solids, and are stripped. The stripping operation is a distillation step that involves heating the material to a temperature commensurate with the desired recovery, yet low enough to prevent cracking. The vaporized hydrocarbons from the stripping operation are condensed as salable product and the remaining liquid consisting of heavy hydrocarbon fractions and solids are pyrolyzed. The pyrolysis step involves heating the material to considerably higher temperatures to recover more light hydrocarbons and to convert the material to a solid residue. Some of the light hydrocarbons produced during pyrolysis are condensable and can be recovered as liquid product and sold, and some are gases that can be used as fuel for the process.

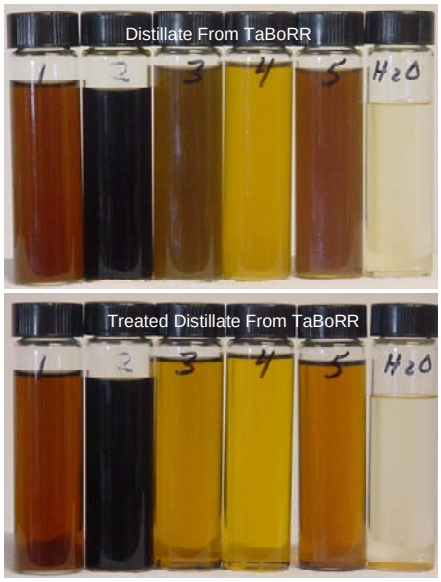
During the course of this Cooperative Agreement, a series of tasks were undertaken to support various aspects of the TaBoRR technology and its variation for use as a heavy oil upgrader, the WRITE (WRI Thermal Enhancement) technology.

Under tasks 1.3, 3.1, 3.2 and 3.6 experiments were conducted to determine the efficacy of the TaBoRR and TaBoRR-like treatment options for recovering salable products from used motor oil and by co-processing used motor oil with waste plastics. For the motor oil application, the laboratory-scale tests performed showed that up to 80% recovery of hydrocarbons is possible in the stripping operation. Stripper bottoms produced were then pyrolyzed in a six-inch twin-screw pyrolyzer. The bench-scale pyrolysis tests showed that 45% of the pyrolysis feed reports as a liquid product, and about 40% as gas. Nevertheless, solids produced from other materials tested in a similar fashion, when subjected to Toxicity Characteristic leaching Procedure for Resource Conservation and Recovery Act elements, passed these tests. During pyrolysis the heavy hydrocarbons are converted to coke. The process tends to encapsulate the solids (inert particulate matter such as wear debris in the motor oil) and hence reduce their leachability/mobility.

The discovery that solids produced from the pyrolysis of the hydrocarbon stream are encapsulated and rendered inert by a coke layer led to the development of work scope carried out Under Task 3.3. Equipment was assembled to allow pyrolysis of the contaminated soils in the TaBoRR facilities. This expanded the application regime of the TaBoRR technology to the remediation of contaminated soils, as well. Processed materials were thereby land fillable reducing the overall remediation and disposal costs.

Pyrolysis reactions involving coking and cracking, in refinery processes, the TaBoRR pyrolyzer, and the WRI plastics/heavy oil recycling process produced a distillate that contained high concentrations of olefins (alkenes). Olefins are chemically reactive, and if not stabilized, undergo chemical reactions to form high molecular weight, insoluble gums, and precipitates reducing the shelf life of the product. The conventional approach to stabilizing these olefins is through hydrotreating the olefinic double bonds with high-pressure hydrogen and the aid of a catalyst. However, this may not be a viable solution for pyrolysis processes such as TaBoRR and plastics recycling, which may be located away from refineries. The cost of the hydrotreater and supporting units to hydrotreat olefins will add significantly to the capital, operating, and maintenance costs of the basic process. This may destroy any economic advantages of pyrolysis processes. Under Task 3.4, alternative approaches to remove olefins from pyrolysis-produced

distillates were identified and investigated to support the development pyrolysis-based technologies such as TaBoRR, WRITE and co-processing of used motor oil and plastics.



The objective of the research under Task 3.4 was to identify and evaluate chemical procedures that could be used to transform olefins formed during pyrolysis into less reactive species without the use of high-pressure hydrogen.

The hydrogenation studies using the model compound blends showed:

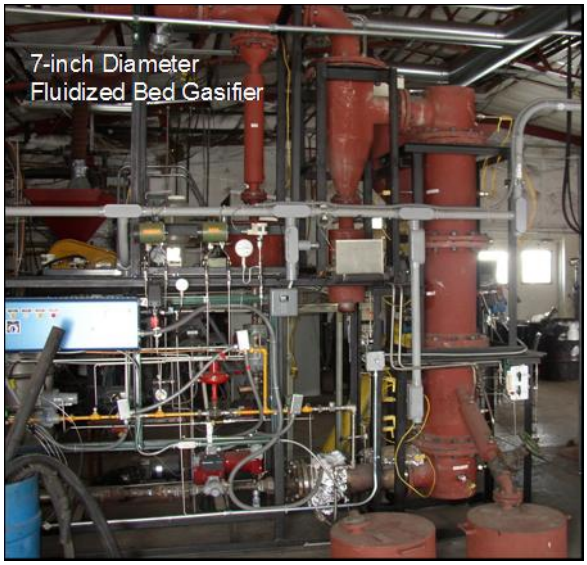
- Air oxidation of the model compound blend showed 22% removal of olefins. This was primarily from removal of 2,4,4-trimethyl-2-pentene and 4-methyl-1-cyclohexene.
- Supplying hydrogen with a donor solvent at 350 °C (662 °F) showed olefin removal of 64%. Reduction of olefins by hydrogenation from a donor solvent results in olefin removal to the extent that it could be a useful method.
- Friedel-Crafts reactions using montmorillonite clay as the Lewis acid show 98% reduction of the total olefin concentration. Based on the model blend results, this method is very attractive.
- Reduction of double bonds with diimide generated from the thermal decomposition of p-toluenesulfonhydrazide (TSH) at 108 °C (226 °F) resulted in 95% removal of the total olefins. Reduction of the olefins with diimide is also an attractive approach.

Three of the procedures (air oxidation, Friedel-Crafts alkalation, and diimide reduction) evaluated with the blends of model compounds were further evaluated using the pyrolysis-produced distillate. The major findings from this effort are as follows:

- The reduction in the olefin concentration using air oxidation was low, only 6%. Although there was an observed removal of olefins, it was not considered to be significant and air oxidation does not appear to be a viable procedure.
- The removal of olefins by Friedel-Crafts alkylation ranged from 5–9% over a reaction time range of 1–8 hours. The low level of removal of alkenes from distillate was surprising when the results from the model compound studies were considered. Friedel-Crafts alkylation, therefore, is not an effective procedure for removal of the type of olefins present in this distillate.
- Reduction of the olefins with diimide used p-toluenesulfonhydrzide as the source for diimide showed a maximum removal of olefins from the distillate was 65%. Diimide reduction of the olefins appears to be the most effective method for olefin reduction.

Combustion and Conversion Technologies for Western U.S. Coals
Tasks 1.5, 1.E, 1.I, 1.J and 3.5

Tasks proposed addressed the specialized processing needs of the direct utilization and conversion of western U.S. coals in advanced power systems. The utilization schemes being developed and tested rely on the fact that western U.S. coals can be "partially" gasified at relatively low temperatures, and that the concomitant char produced is reactive. These characteristics afford western U.S. coals a significant advantage over bituminous coals and solid waste fuels such as petroleum coke. However, one of the major issues facing such utilization of coal is the arrival of vapor-phase ash constituents that can cause fouling and hot corrosion of gas path components.



As part of this project, WRI constructed and tested a fuel-flexible gasifier. The seven-inch diameter, fluidized-bed gasifier was designed to be operated as an air-blown, enriched air-blown, oxygen-blown, or as a steam pyrolysis unit. A series of cold-flow fluidization tests was performed with a bed of Wyodak coal in the 1/16”-1/8”size range. Observation of the bed allowed the fluidization regime to be determined for ambient pressure, ambient temperature operation. Hot-flow tests were performed at 1200 to 1450ºF range, to assess the fluidization behavior at temperature. Analysis of the syngas product allowed an optimum air/coal ratio to be identified. These data were reported in a topical report.

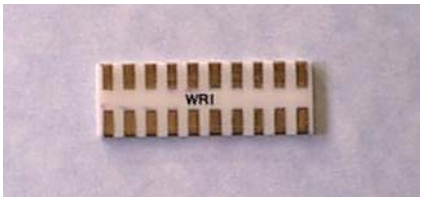
The fluidized-bed gasification unit then became a test bed for additional Base Program and JSR Program testing. An engineering design was completed to overhaul the sampling system. Upgrades included particulate filtration, and provisions for drying the gas stream. The modified system works across a broad range of temperature and pressure conditions to allow for more flexible test plans. The system can provide syngas for testing in the 5 to 200 ºC range, and at pressures up to 300 psig.

The improved gasifier has been used for a number of different experiments. During mercury adsorption experiments, Task 1.E, the gasifier was operated for six working days for a total of approximately 30 hours of sorbent exposure time on super-activated carbon at temperature. The results showed that acidified carbon was more effective than activated carbon for elemental mercury removal from syngas. The coal gasification system has shown to be extremely useful as a flexible source of synthesis gas. JSR and client-funded projects are using

the synthesis gas produced as a slipstream to test hydrogen separation and water gas shift catalysis.

Task 3.5 addressed the development of a real-time on-line alkali monitor. The underlying principle for the on-line probe was the determination of the dew point of the vapor phase compounds. Once the dew point had been established the concentration could be deduced from the available thermodynamic equilibrium data. Two different detection methodologies were identified for testing (a) Electrical Conductivity Measurement (ECM) Technique that relies on the fact that molten salts are better electrical conductors than their solid counterpart, and (b) Electrical Resistance Measurement (ERM) Technique which is based on the fact that molten alkali compounds do cause very high corrosion rates in several different families of heat resistant metallic alloys.

The second method for sensing the presence of a molten layer of alkali compounds required a complicated sensor/reference element arrangement, whereas the first method offers the possibility of a relatively compact sensor almost in the shape and form of a printed circuit on an insulator, such as an alumina wafer.



A series of crucible experiments were used for proof-of-concept verification. A simple two-conductor probe was assembled from gold wires. The electrical resistance of the probe was measured by immersing the tips of the gold wires in alkali salts. A multi-element probe was then fabricated and underwent verification tests. The probe consisted of eight 1-mm wide gold stripes painted on a 35 mm x 13 mm x 2 mm alumina wafer. The gold stripes ran along the width of the wafer and the separation between the stripes was about 1 mm. Gold wires were attached to the gold stripes by mechanical means. The alumina wafer was assembled onto an air-cooled stainless steel block. Eight type K thermocouples were used to monitor the temperature of the wafer from the backside.

Verification tests conducted, used a deposited layer of an alkali compound or a mixture. The compound(s) was dissolved in water and then a thin layer of the solution was painted on the alumina wafer covering the gold stripes and the intervening gaps. The wafer was allowed to dry and then the entire probe assembly was installed in the furnace. Probe response as electrical resistance between neighboring stripes and the temperature profile of the wafer was recorded as the furnace temperature was increased to temperatures greater than the melting temperature of the alkali compound or mixture. When a stable temperature profile was achieved the resistance map of the stripes was used to detect molten salt. The probe assembly could easily detect a change in the solid to liquid phase.

A test setup was constructed whereby alkali-laden gases could be contacted with candidate materials of construction. The setup consisted of gas metering and blending equipment, furnaces for heating and cooling the gases and test samples, and associated monitoring and control assemblies. Alkali vapor pressure was controlled by placing a known amount of the compound in the high-temperature zone of the furnace. A small sweep gas velocity was used to transfer the vapors to the lower temperature end of the furnace. All test fixtures and probe assemblies were to be exposed in the lower temperature zone. This arrangement was needed to ensures an equilibrium vapor pressure of the alkali compound commensurate with the operating temperature of the lower temperature zone of the furnace.

Further testing and development on the project was halted because of lack of funding for the second year of work. Nevertheless, the work completed led to a patent on the sensing scheme.


WRI's 250,000 Btu/h Combustion Test Facility

Coal combustion technologies that make coal combustion cleaner and more environmentally efficient are receiving a great deal of attention in the industry. Under Task 1.J, several projects were completed to upgrade the capability of the coal Combustion Test Facility. Each of the four coal feeders was replaced by an auger type device. External electric vibrators were added at the upper tee to reduce coal clogging. Air velocities and piping sizes have been found to be critical to smooth coal delivery. The induced draft fan that handles the flue gas was retrofitted with improved seals to allow better measurement of mass balances and reduce the potential for flue gas leakage. The four coal feeders were upgraded with individual weight loss balances to allow continuous monitoring of coal feed rates. The newly installed system continuously data log coal feed rates and account for feed rate changes. The lower section of the CTF furnace was recast with refractory. Other upgrades included the QSIS probe (Quick Silver Inertial Separation) for mercury analysis was replaced. The QSIS probe is an essential device for separating the fly ash from the sampling gas located upstream of the back-pass for an accurate mercury measurements. A perforation in the original device was attributed to the acid gas in fly ash and the high velocity required for ash disengagement over this full duration of service life.

As a result of these changes, the coal combustion test data are now more consistent. Several commercial clients are collaborating with WRI to test and develop air pollution control technologies that would ultimately be applied to coal-fired power plants. List of recent clients include BOC, Linde, Mobotec, Idaho National Laboratories, Fuels Management Inc., Adaro, BHP Billiton, Headwaters, KFx, Evergreen Energy, Hydrogen Technologies Inc., Breen Energy and others.

Technical Assistance and Technology Transfer Programs
Tasks 1.9, 1.L, 2.2, 3.6, and 3.E

The goal of the tasks under this Program was to establish a program that could provide technology transfer to the energy producers in the Western US.

Under Task 1.9, this Program unsuccessfully attempted to develop a consortium of oil and gas producers. A mass mailing was conducted to independent operators along the Front Range seeking input on the need for a consortium to define R&D needs. The mailing also introduced them to WRI and our ongoing DOE-sponsored programs in the Oil and Gas extraction area. From the feedback, it was realized that need for such services was quite sparse. Further efforts to organize the independent producers were abandoned.

Under Task 3.E, based on WRI's long-standing presence in the subbituminous coal industry, a coalition of the coal producers and users was successfully formed, Subbituminous Energy Coalition (SEC). At the time SEC was formed, Environmental Protection Agency (EPA) had promulgated mercury control regulations on coal-fired power plants which then brought out the specialized problems and needs of the subbituminous coal industry. Like the lignite coal industry, the subbituminous coal-fired power plants have the vast majority of their mercury in the flue gas in the form of elemental mercury, while the eastern bituminous coal-fired power plants have the vast majority of their mercury in the flue gas in the oxidized form. Working with SEC members, this task addressed the coal industry's need of technical support and assistance. Information exchange forums and sessions were organized. From its modest beginnings, the SEC now has over 50 members. On the mercury issue, the SEC was an effective voice for the subbituminous coal industry in commenting on the proposed regulatory actions by EPA. Recently, the SEC has included the issues and challenges of the climate change / greenhouse gas emissions / CO2 capture and storage in its working agenda. Outreach efforts under the Cooperative Agreement have been very successful in providing forums for the industry to share information, technology transfer, organize a consensus of the industry for regulatory comments, and jointly developing future plans for industry.

As a part of the technology transfer activities, Under Tasks 3.6 and 1.L, WRI collaborated with NCUT to cosponsor the 3rd and the 4th Upgrading and Refining Conference in Edmonton, Alberta, Canada. Working with NETL, WRI was responsible for providing a Keynote Speaker for the Conference. Nearly 300 delegates attended the 4th Conference where 32 papers technical were presented. In addition, WRI organized a workshop on Corrosion and Fouling in the refinery equipment. The workshop was also well attended.


Attendees at the Heavy Oil Upgrading Conference

Oil and Gas Production
Tasks 1.7, 1.A, 1.G, 2.B, and 3.F

Under this Cooperative Agreement, the effort in this area had been only to complete the work that began under prior agreements. Under tasks 1.7 and 1.A, WRI's enhanced CBM production methodology was completed. Several modifications were made to WRI's coalbed methane simulator (WRICBM) that improved its predictive capability. The modifications included: (1) providing a variable thickness feature, (2) adding the ability to specify under saturated coal either by constant saturation pressure or as a function of initial reservoir pressure, (3) adding three-dimensional cylindrical grid, and (4) adding an improved function for calculating the viscosity of gas mixtures as a function of reservoir pressure. A consultant performed an independent evaluation of the WRICBM. The consultant found that WRICBM gave results that were comparable to commercial simulators for single and multi-component sorbed gas systems. A history match study was performed for the Powder River Basin of Wyoming. The study matched pressures and used proprietary reservoir and production data. The study resulted in a sorption isotherm that was significantly different than is typically measured in the laboratory from extracted coal cores. These results suggested that extracting coal to the surface using typical coring methods might alter the coal's ability to hold and release methane. As a result, Task 1.A was initiated to evaluate various techniques that might provide in-situ sorption/desorption isotherms for methane in coal. Work in this area was abandoned when the PIs left WRI.

Under Tasks 2.B and 3.F, the extent of the volatile organic compounds (VOC) pollution from the oil production and storage facilities was assessed. In the production sequence for oil, the oil is pumped from the well to an initial storage tank or tank battery. These tanks generally have hatches on the top that allow a limited amount of pressure to build up before it is vented to the atmosphere. The pressure buildup is caused by the liberation of VOC that were originally dissolved in the oil at the formation temperature and pressure. The release of VOCs from one tank is generally not significant, but the combined release from several tanks in the same general area could be substantial. This problem was identified by the state environmental regulators in Colorado that the VOC emissions from the oil and gas sites in Weld County, Colorado, northeast of Denver, are greater than the pollution from factories, power plants, and refineries in the region and close to the total emissions from all cars and trucks operating in the Denver metropolitan area.

The objective of the tasks 2.B and 3.F was then to evaluate and select technologies for controlling the VOC discharge from oil field production and storage facilities. Working with several small-and medium-size oil producers along the Front Range, emissions data were collected. The project activities then culminated into a Jointly Sponsored Research Project whereby working prototypes were tested to control the fugitive VOC emissions from the oil-field production equipment.

Catalysis and Synthesis/Liquid Fuels
Tasks 1.D, 1.F, and 2.9

Under the auspices of the Cooperative Agreement, WRI began the development of synthesis technology to convert syngas to a mixture of alcohols. Consistent with the DOE interest in furthering the technologies for the production of transportation fuels from alternate sources such as natural gas, biomass and coal, mixed alcohols represented a way to replace MTBE as the oxygenate gasoline blend. The first step of these processes is the production of synthesis gas; the second step of these processes is a catalytic conversion of synthesis gas to alcohols or other fuels.


Catalyst Testing Facilities at WRI

Under Task 2.9, development of a catalyst with selectivity for ethanol and higher alcohols was undertaken. Catalyst production and testing facilities were developed including fixed-bed, slurry-bed and fluidized-bed synthesis reactors. The catalyst developed produces predominately straight-chain terminal C1-C6 alcohols, a similar product to the DOW catalyst discovered in the mid 1980's and the PEFI catalyst tested in the early 2000's. However, WRI's catalyst has a key advantage because no sulfur containing byproducts are produced, a potentially serious issue for sulfur containing catalysts. WRI has filed a patent application for the catalyst formulation.

The process is an outgrowth of a long-term development project in Fischer-Tropsch (FT) chemistry. On the basis of the previous work, the data also indicate that the yield can be nearly two times that of the conventional Fischer-Tropsch synthesis. The principal use foreseen for the alcohol mixtures is as a high-octane blending stock (10% or higher) for gasoline. It is expected that the mixed alcohol product, essentially denatured ethanol, will also make a high powered, clean burning fuel, either neat or in an 85% blend with gasoline. The availability of the co-product, higher alcohols, may offer chemical producers and refiners an attractive way to use synthesis gas particularly that produced from isolated natural gas sources. Similarly, synthesis gas from various waste materials, such as biomass from municipal solid waste (MSW) or refuse-derived fuel (RDF), and coal can become chemical feedstocks.


Catalyst Preparation Set-up

Under the Jointly Sponsored Research Program, the mixed alcohol synthesis technology is being scaled-up to 50 gallons per day pilot facility. Under the auspices of Task 2.9, equipment for scale-up production

methodology was developed to meet the catalyst needs of the pilot plant.

The mixed alcohol synthesis process offers several advantages over conventional FT synthesis. Sulfur poisoning of the catalyst is a major problem in a number of other processes and usually requires a reduction in the sulfur levels in the synthesis gas before it can be admitted to the reactor. The catalyst formulation for this process is sulfur tolerant and hence such a conditioning step is not critical. The product from this catalyst requires very little treatment to be used as a motor fuel, probably only dewatering. FT processes require the equivalent of a mini refinery to convert the product to a usable motor fuel.

Under Task 1.D, the use of WRI catalyst for direct coal liquefaction was explored. A review of the prior art indicated that economics may not be favorable for the approach.

Under Task 1.F, use of ionic liquids, organometallic salts, was explored as a slurry medium in a slurry bubble column catalytic synthesis reactor. Ionic liquids have many useful chemical applications. They have been used as novel solvents for organic synthesis, in liquid extraction, in electrochemical studies and in some cases as catalysts. The unique combination of properties such as extremely low vapor pressures and unusual and adjustable solvent characteristics present the possibility of developing "designer solvents" for particular applications. In addition, ionic liquids can have stable liquid ranges of over 300K between melting and boiling points. The objective of this work was to identify and or develop ionic liquids for Fischer-Tropsch (F-T) synthesis. For F-T applications, specific desired properties of ionic liquids are: (1) excellent thermal stability and low vapor pressure over a wide range of temperatures, (2) high solubilities for carbon monoxide and hydrogen, (3) good heat transfer properties to allow control of exothermic reactions, and (4) low solubilities for desired products in order to drive the reactions toward completion (Le Chatelier's Principle). Low solubility for products will also simplify separation of products from the catalyst. Separation of products from the catalyst slurry is a particular problem in conventional F-T applications. In addition to the solvent properties of ionic liquids, the incorporation of metals offers a unique possibility - the solvent also serving as a homogeneous catalyst. Based on these considerations we identified potassium formate as a low cost likely heat transfer fluid which is an ionic liquid at temperatures used for synthesizing alcohols in an F-T type reaction scheme. However, actual tests indicated that, when compared to hexadecane, the benefits were non-existent.

Coal Bed Methane Produced Waters
Tasks 2.1, 2.7, 2.A, 2.F

Water quality issues are at the forefront with regard to the development of coal bed methane (CBM) reserves in the Powder River Basin (PRB). The practice of discharging large volumes of water into drainage channels or using it to irrigate rangeland areas has the potential of causing serious problems with regard to salinity and sodicity of soils. Some waters currently disposed of in the PRB are of such quality that land application should not cause any significant

problems. However, there is evidence that some of the CBM-produced waters will cause problems with salinity and sodicity.

Under task 2.7 WRI evaluated the chemistry of produced waters generated at various locations in the Powder River Basin with regard to salinity and sodicity and determine how such waters will impact the physical and chemical nature of soils in the vicinity of active production.

The primary problems associated with salinity are related to the ability of plants to take up water to facilitate the biochemical processes of photosynthesis and plant growth. As the solution electrolyte concentrations of the soil increase, plants dependent on their level of salt tolerance will become less able to absorb the amounts of water needed. As a result, plants are not able to function at high levels and will grow at slow rates or die.

The major impact of sodicity on soils is associated with soil structure. Soil structure is important to maintain the flow of gases (oxygen) and solution (water plus nutrients) to plant roots. Sodicity can cause severe erosion of once-productive soils. Depending on the characteristics of individual soils, as the level of sodium in the soil increases, the physical structure will degrade. High levels of sodium can cause the structure of a soil to completely disperse.

An important aspect of the sodicity (SAR) and salinity (EC) chemistry of soils is that the two are closely related. For example, a highly sodic (high SAR) soil can maintain its soil structure if the salinity level (EC) of the soil is high. However, if the salinity level is low (the water is very clean), the highly sodic soil will slake and disperse and the structure will be lost. If a soil is characterized by a low SAR, the application of clean water or water characterized by low EC can cause degradation of the soil structure. If the electrolyte concentration of the water applied to the soil is high (EC 2 to 3), the soils will maintain their structure.

The dilemma of this system is to make sure that water applied to soils meets the favorable combination of salinity and sodicity that will allow the plants to grow at good production levels and maintain the structure of the soils. Each soil will react differently to the chemistry of the water applied and the method of application. Therefore, the research effort that includes studies of the interactions of these various parameters with the soil types found in the area should be conducted so that produced water from CBM operations can be discharged in an environmentally safe manner.

The overall objective of Task 2.1 was to evaluate the feasibility of using colloidal gas aphrons (CGA) flotation for the cleanup of metals-contaminated water. Three criteria were used for the evaluation: metals removal, estimated cost, and sludge volume. Experiments were conducted to provide preliminary data with which to assess CGA flotation in terms of these three criteria. A series of lab-scale tests demonstrated that colloidal gas aphrons were indeed useful in

remediation of waters contaminated with metals. For example, more than 99% of the iron present in the samples tested was removed by this treatment.

Under task 2.A, techniques for removing barium from the CBM produced waters were investigated. Treatment of the water with soluble sulfate sources such as gypsum was determined to be effective for barium attenuation.

Under Task 2.F, Enhancement of Biogenic CBM Production and Back Injection of Coal Bed Methane (CBM) Produced Water, The focus of the work was to enhance biogenic methane production from coal, oil shale, and other carbon rich materials (e.g., lignite, peat, and diesel-contaminated soil) by optimizing chemical and physical parameters in bioreactors established in the laboratory with long term goals focused on revitalizing played-out CBM wells. An explicit related outcome of this work was that similar techniques could be applied to extracting energy from oil shale through in situ bio-gasification (methanogenesis).

Methane (CH4) is a common constituent in deep subsurface environments, often formed through thermogenic and biogenic (methanogenic) processes. Approximately 20 to 40% of all methane on earth was likely generated through biogenic processes with even higher concentrations (up to 65%) under optimal bio-geological conditions. Actual biogenic methane production is accomplished by methanogenic Archaea (methanogens), which thrive in strictly anaerobic environments with available CO2 (CO32-, HCO3-) and acetate and low sulfate concentrations at temperatures ranging from 9 to 110ºC. Methanogenesis results in the reduction of CO2 to form CH4 with sufficient small organic molecules and H2.

Recent isotope work has indicated that the majority of methane produced from coal bed methane (CBM) wells in the Powder River Basin (Wyoming) was formed biogenically unlike eastern methane reserves which are primarily thermogenic, this difference reflects the higher bioavailable carbon concentrations associated with western coals as opposed to eastern coals. Methanogenesis has also been demonstrated in deep subsurface oil-bearing sedimentary rock such as oil shale. One problem the oil and gas industry faces regarding methane reserves is the relatively short life span and transitory nature of these resources. For instance, CBM wells typically have a life span of less than 10 years after which time the available methane has been removed and the well is capped and abandoned leaving enormous concentrations of available carbon in the subsurface that could potentially be converted to methane.

Data from baseline chemical and microbial characterizations of coal and oil shale were used to calculate appropriate nutrient and chemical amendments. Various pressurized and non-pressurized reactors were amended with different mixtures of nutrients (e.g., nitrogen and phosphorus amendments), acid and base treatments, and bacterial inhibitors, and held at varying temperatures. Head-space analysis from each reactor was used to calculate total methane and CO2 concentrations.

Results indicated that the addition of nutrient amendments can enhance biogenic methane production from coal and oil shale. Methane production rates from oil shale were as high as 1.63 µmol/d/kg, while coal produced 0.09 µmol/d/kg. The higher rate of methane production from oil shale is likely due to the larger amount of bioavailable dissolved organic carbon (DOC) in the shale. Additionally, the project determined that it may be possible to pre-treat coal by raising the pH to basic levels to yield larger amounts of bioavailable DOC. This suggests that the higher bioavailable DOC concentrations in oil shale may be due to its basic pH when saturated in water (as high as 9.9). Chemical pretreatment and temperature and pH optimization are needed and have been shown with oil shale (JSR Task 69) to enhance biogenic methane production producing very low concentrations of CO2.

In summary, Task 2.F has successfully demonstrated that enhanced biogenic methane production is possible within a suitable time frame to contribute to current energy demands.

Beneficial Uses of Coal Combustion Products
Task 2.3, 2.C, 2.G and 3.7

Coal combustion products (CCPs) represent a large-volume waste that is produced by the electric utility industry and less than 25% are utilized in the production of usable products. The major recycling application of CCPs is the production of concrete as a cement replacement.

Under Task 2.3, WRI examined the use of dry flue gas de-sulurization (DFGD) ash in the production of various construction applications. The results of testing indicated that there was likelihood that the Class F ash in commercial rapid-setting flowable fills could be replaced with DFGD ash, thereby resulting in a marketable fill material for excavatable applications. Class F and Class C ashes are currently combined to produce a commercially available flowable fill material. The DFGD ashes represent the ashes generated from the combustion of coal, which without DFGD, would produce either a Class F or a Class C ash, hence the use of the nomenclature of a Class C DFGD and Class F DFGD. DFGD ashes are produced throughout the United States and, in particular, in the Rocky Mountain region.

As a part of the work completed under Task 2.3, WRI conducted an investigation of the geotechnical and environmental impacts of substituting DFGD ash for the Class F ash in flowable fill applications. The results of the investigation concluded the following:

- Flowable fill material can be produced with geotechnical properties similar to current Class F/Class C flowable fill materials, including handling characteristics and ultimate strength.
- The leachate characteristics of the DFGD ash-based flowable fill materials are similar to conventional flowable fills and meet the EPA limits for metals constituents.

- The impact of DFGD ash-based flowable fill materials on potential embed materials has been tested representing decades of service without any indication of corrosion or other detrimental impacts.

The use of DFGD ash in the production of flowable fill for excavatable applications appeared to be technically feasible.

The goal of work conducted under Task 2.C was to provide an assessment of the technical and economic benefits of the use of commercial polymers in ash management and construction applications. The specific objectives were to provide technical assessment of use of polymers in ash-based materials and to assess the technical benefits of polymers in high-value ash management applications. Work proposed included preliminary testing of a range of polymers in combination with Class C and Class F ashes. Technical properties of the green and hardened ash and concrete-ash products were to be determined by WRI and by Dow-Reichold. Early testing demonstrated that the two laboratories could not reproduce each other's results. Equipment upgrades were warranted to alleviate the discrepancies in the test data. Lack of adequate funding precluded further continuation of this work.

Under Task 3.7, the scope of WRI's CCP work was expanded to include the incorporation of lignin, a by-product of biomass processing. Lignin and other biopolymers are not soluble in water, are sufficiently hydrophobic, and are also not readily dispersed in water. Therefore, lignin must be modified before it can be successfully used in formulations with CCPs to produce ash-based building materials. Under this task, several approaches were evaluated including supercritical alcoholic water, high-pressure liquid water, and caustic solutions.

All of the approaches tried indeed digested commercially available lignin. However, none of the approaches produced a product that had sufficient water solubility to allow lignin incorporation into CCP-based products.

Under Task 2.G, WRI assessed suitability of CCP technologies developed under both the Base and the JSR Programs, for the emerging International markets in China and India. Both of these countries have experienced high growth in power needs and resultant ash generation. In both the countries, coal quality is poor and as a result ash quality does not meet C-318 specifications. In addition, many of the existing plants and all of the new plants are installing

some level of SO_2 control, thereby resulting in high calcium and sulfate ashes that are prone to expansion without proper handling and treatment. Major differences in the coals being used for power generation, preclude direct application of technologies developed for the US CCP.

Biomass Processing
Task 1.B, 3.7 and 3.G

Under the Cooperative Agreement, WRI conducted some research in the use of biomass as an energy source. Three small tasks were concluded under the Base Program. The most notable effort in the area was undertaken by Task 3.G which ultimately led to a JSR project.

Lignocellulosic biomass, such as wood chips, corn stover and wheat straw are attractive, low value feedstocks that are composed of the biopolymers: cellulose, hemicellulose and lignin. Cellulose is the important component in lignocellulose for the production of ethanol because it is a biopolymer of glucose, the sugar needed for fermentation to produce ethanol. Direct conversion of low-value biomass to transportation fuel (ethanol) has not been a commercially viable approach because of the problems encountered in degrading the lignin. As a result chemical treatment and pretreatment approaches are employed to either convert the biomass to soluble components (strong acid hydrolysis) or to fractionate the biomass to yield the individual biopolymers. Strong acid hydrolysis is effective at reducing the biomass to soluble components, but inhibitory materials (furfural) are produced that adversely affect down stream bioprocesses.

In addition, enzyme hydrolysis of the cellulose, as proposed in many biorefining concepts, is a slow reaction that is further encumbered by the cost of the enzymes, which can only be used once. To avoid these reaction limitations, large tankage volumes are required to provide the throughput necessary to accommodate the anticipated low sugar concentrations. This adversely affects the economics of the process. As a result of these deficiencies, Under Task 3.G, WRI investigated alternative approaches to lignocellulose biomass pretreatment and conversion to lignin and sugars. Bench-scale pretreatment experiments were conducted with wheat straw.

Major findings of the research conducted were:

- The biomass pretreatment process, consisting of digestion of lignin in water and ethanol coupled with steam explosion, was found to remove 90+ % of the lignin. Enzymatic digestion of the cellulose showed that in excess of 80% of the cellulose could be digested to produce glucose.
- Cellulase enzymes were immobilized on an inert support and it was determined the maximum amount of enzyme that could be immobilized was 430 mg (enzyme)/g support.
- Repeated recycling of the supported catalyst consisting of using the catalyst for cellulose hydrolysis, precipitation and collection of the catalyst, and using the recovered catalyst for enzyme hydrolysis, showed the catalyst could be recycled twelve times before the

enzyme activity decreased below 80% of the initial activity. In a commercial process, the increased enzyme life equates to six weeks of use as compared to 5 days for the unbound enzyme.

As described earlier in this report, work conducted under Task 3.7 included development of dissolution techniques for lignin for its ultimate use in the CCP utilization.

Task 1.B involved the treatment of biomass with bromine. The underlying concept was to use the bromine as a strong oxidant to strip and recover hydrogen from the biomass which could then be electrolyzed. Small scale experiments conducted in the laboratory showed that the concept involving hazardous chemicals will probably not be economical.

HAPs Emissions and Mitigation
Tasks 2.4, 2.H, 2.K, and 3.H

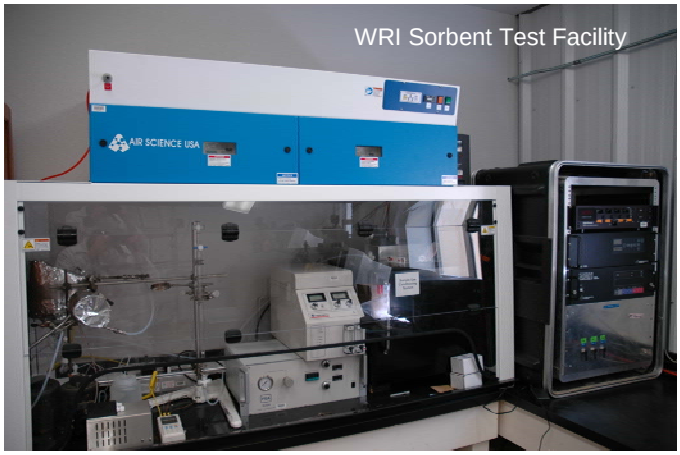
The 1990 Clean Air Act Amendments and the Environmental Protection Agency's review of hazardous air pollutants have prompted development of technologies to remove mercury from coal or reduce mercury emissions. To address the need for a cost-effective mercury removal technology, Under Tasks 2.4 and 3.H, WRI is developing a patented (U.S. Patent No. 5,403,365 - "Process for Low Mercury Coal", Merriam 1995) mercury removal technology based on thermal pretreatment of feed coal. Earlier research at WRI demonstrated that approximately 75% of coal-bound mercury can be thermally evolved from dried Powder River Basin (PRB) coal at temperatures below 290°C (554°F). WRI is currently developing and validating the process at the process development level for application in the power plant. Plans are underway to demonstrate the technology at a power plant scale.

Under Task 2.4, WRI performed bench-scale testing of the underlying concepts of a technology to remove mercury from low-rank coals before their utilization. Test data defined the optimum processing conditions with respect to the temperature, residence time, and sweep gas flow rates. The work completed under this task was used to develop a multi-client Jointly Sponsored Research project to further develop the technology.

Task 3.H complemented the work conducted under Task 2.4 and that under the JSR project, by evaluating the means for stabilizing the dried, reduced mercury product from the WRI's process. Stabilization is an important step so that off-site processing can be undertaken in those cases where retrofit space in the power plant might be limited (e.g., at the mine or a site adjacent to power plant). Without some way to stabilize the dried coal product, the storage and shipment of dried low rank coal are subject to dusting, moisture re-adsorption and spontaneous combustion. Under Task 3.H, WRI evaluated an NETL proprietary technology for stabilizing the product from WRI's thermal treatment process. Based on bench-scale testing some beneficial effects were indeed derived for both the sub-bituminous and lignite coals. However,

the benefits for larger coal particles were limited. Similarly, an economic evaluation of the treatment process for showed the economic viability to be marginal.

Looking to the future regulations of emissions from coal-fired power plants, Task 2.K was conceived to develop and test sorbents for the removal of mercury at temperatures above 500ºF, that can also remove As and Se as well as Hg. Multi-pollutant sorbents that can operate at high temperature, and which are cheap, thereby allowing once through use, will find a market in both pre-and post-combustion applications, as well as in gasification systems. The objectives of Task 2.K were to develop and test low-cost, once through formulations of non-carbon based sorbents that are capable of capturing multi-pollutants (i.e., As, Hg, Se) at high temperatures (~500 degree F) in oxidizing and reducing environments (combustion and gasification).



As a part of this task, a sorbent test facility has been assembled and commissioned. The design of the facility is flexible enough to allow testing of sorbents for the utility industry today as well as in the future. Various sorbents can be tested under different conditions, such as novel non-carbon based high temperature sorbents that can capture metals as Hg, As and Se either from the flue gases at a power plant, Syngas from gasification systems, or the sweep gases from pre-combustion processes, such as WRI's process for upgrading coal.

Task 2.H in this area assessed the potential mercury emissions from oil-shale processing. Laboratory heating experiments were conducted on small samples of western oil shales to typical processing conditions. The results showed that oil shale from each of the three principal western oil shale producing states have potential issues with mercury loss to the environment during processing. This mercury emissions level is likely to be significantly higher than for western coal producing the same energy value. Both above ground and in-situ processing is likely to emit mercury with the gas phase material produced. All experiments showed the mercury in the gas phase as elemental vapor. Nevertheless, it should be pointed out that products and processes do exist to deal with mercury vapor in gaseous emissions.

VOC Sampling and Sample Storage
Tasks 3.8 and 3.D

Under Task 3.8, WRI proposed the development of a field portable kit based on refrigerant leak detector technology for screening halogenated volatile organic compounds (HVOCs) in the field. Both corona discharge and heated diode refrigerant leak detectors were to

be evaluated for potential utility for quantitative screening for HVOCs. Under this task following extensive baseline testing, heated diode leak detectors were modified and assembled into units with rapid response and enhanced sensitivity, and on-board digital readout. For the field-deployable units, the limit of detection for trichloroethylene (TCE) in air is 0.1 mg/m^3 (S/N = 2). The response to other HVOCs relative to TCE is similar. Variability between sensors and changes in a particular sensor over time can be compensated for by normalizing sensor readings to a maximum sensor reading at 1,000 mg/m^3 TCE. The device is ready for commercial production and is the subject of a JSR project.

Task 3.D developed an integrated freezer system that uses a frozen phase change liquid (PCL) formulation in specifically modified coolers to maintain freezer temperatures for shipping environmental samples from the field to the laboratory. Current practice for storing samples for shipment is to pack them in dry ice. However, air shipment of packages in dry ice is forbidden. As a result there is a need for a new freezer system. As a part of this task, based on a series of laboratory evaluations, a phase change liquid composition was optimized. The PCL was then integrated into cooler. Experiments were performed using various cooler types packed with soil samples as would be done in the field for sample shipment to a laboratory. Experimental results showed the importance of the type of cooler used in the system and that an optimal configuration of the insulating material within the cooler improves the performance of the freezer system. In this testing, an integrated freezer system containing soil samples was shown to maintain temperatures at <-7 to -20 ºC, the temperature range specified for frozen samples by the U.S. EPA, for 47 hours. The results are very promising such that commercializing of the new sample storage and shipment technology is being pursued under a JSR project.

Advanced Remediation Technologies
Tasks 2.5, 2.D, 2.E, 2.I, and 2.J

Tasks in this group addressed the environmental issues of energy production including acid mine drainage, hydrocarbon contamination of soils and water. Advanced remediation concepts involving the use of amendments, specialized treatments including organisms are being explored and demonstrated. WRI scientists are also developing schemes that might someday be able to produce power in conjunction with the remediation efforts.

Task 2.5 dealt with acid mine drainage (AMD). AMD often results from mining operations. The primary formation of acid is the oxidation of pyrite (FeS2) in water that yields ferric hydroxide and sulfuric acid. Ferric iron then further oxidizes pyrite to release more acidity, and continued reactions result in AMD. The AMD mitigation scheme proposed under Task 2.5 was based on depletion of oxygen such that the oxidizing sequence of pyrite and associated generation of acid can be shut down. The unique metabolic mechanisms of sulfate-reducing bacteria (SRB) were proposed as an alternative technique for eliminating AMD formation. The sulfate-reducing process consumes protons, resulting in the rise of pH to the

neutral range. A secondary benefit was also expected from the biofilm produced from the SRB in that the process coats the pyrite surface, preventing it from further oxidation. The precipitates also consume the dissolved oxygen on the surface of pyrite, providing a galvanic protection of pyrite being oxidized; therefore the pH in a mining site may be maintained within the neutral range for a long period of time. The objective of the task was to develop this alternative in-situ method to prevent the oxidation of pyrite, thus reducing acid mine drainage problems.

Laboratory experiments involved AMD water collected from a site in Montana with pyrite added to each treatment microcosm. Corresponding treatments were inoculated with SRB from sediments collected from a lake bottom and different substrates (carbon sources) were compared for their enhancement of SRB. The substrates included sodium lactate, glucose, and corn starch over a range of pH. The results confirmed that AMD can be treated with SRB and pH can be maintained in neutral levels by the formation of a biofilm retarding further conversion of AMD-producing material. Based on the success of the laboratory experiments, a JSR project with Rio Tinto Energy America (formerly Kennecott Energy) is demonstrating the SRB treatment at a coal mine in Tennessee (Sequatchie Valley Coal).

Task 2.D dealt with bioremediation of hydrocarbon contamination. Bioremediation enhances microbial biodegrading activities through adjustments of environmental factors such as moisture, oxygen, and nutrient availability. The key to successful bioremediation is availability of nutrients, especially nitrogen, to enhance microbial activity. Commercially available "slow-releasing" nitrogen sources are available but expensive and in limited supply. Under this task, WRI proposed the use of poultry manure as a cost-effective nitrogen source to enhance biodegradation of petroleum hydrocarbons in soils and groundwater. Based on comparative evaluation of commercial uric acid and poultry waste in laboratory experiments with hydrocarbon contaminated soils, poultry manure was shown to be an effective low cost nitrogen source for bioremediation of petroleum hydrocarbons.

Under Task 2.I, WRI scientists are developing microbial fuel cells (MFC) that will generate electricity concurrently during bioremediation processes. An MFC is a device that harvests electrons from the anaerobic degradation of organic substrates, such as petroleum hydrocarbons, and generates electricity. In bioremediation applications, MFC provides anaerobic bacteria with a solid-state terminal electron acceptor (anode) that transfers electrons originated from biodegradation of these organic compounds to the cathode. At the cathode the electrons are consumed in the reduction of oxygen and protons to water. The entire process then generates a low electrical current. Under Task 2.I the feasibility of using MFC technology to enhance biodegradation of petroleum contaminants in anaerobic environments such as contaminated groundwater and sediments is being tested. The technology has the combined benefits of enhanced anaerobic biodegradation of organic wastes and the potential for alternative energy production.

Over the course of Task 2.I, several tests have been conducted to determine (1) if MFCs can enhance contaminant degradation and remediation, (2) what the optimal conditions for MFC performance are, and (3) what types of alternative catalysts can be used to replace the expensive platinum catalyst currently used in most MFC cathodes to reduce construction costs without adversely impacting the performance. Early data are encouraging and suggest that long-term benefits of the MFC technology in effective bioremediation are indeed possible.

Task 2.J again dealt with bioremediation of petroleum hydrocarbon contamination. The objective of the proposed work was to (a) isolate thermolphilic bacteria from the petroleum-impacted soils collected from warm and arid areas and (b) culture the isolates in a small scale bench system and characterize the product biosurfactant. Biosurfactants reduce surface tension, critical micelle concentration and interfacial tension in both aqueous solutions and hydrocarbons. These features make them candidates for enhanced hydrocarbon remediation, microbially-facilitated oil recovery, and other industrial applications. Limited exploratory work concluded under this task has not yet been able to isolate a biosurfactant from the thermophilic bacteria.

Task 2.E dealt with waste water cleanup. Wastewater generated from industries such as oil refining, coal mining, and CBM production, potentially contain high concentrations of toxic oxyanions. As a part of this task, WRI proposed the evaluation of layered double hydroxides (LDHs) as filter material that removes toxic oxyanions from industrial wastewaters. Due to their large surface area and anion exchange capacities, LDHs are expected to be effective materials for removing toxic arsenic and selenium oxyanions from wastewater streams.

A series of bench-scale tests have shown that LDHs indeed effectively remove As, Se, and other oxyanions (e.g., sulfate) from refinery wastewater. Data also show them to be effective for humic acid that can foul membranes typically used for wastewater treatment. LDHs can also remove harmful bacteria and viruses that may exist in the wastewater. Overall, LDHs in aqueous suspension are quite suitable for treating wastewater generated by the energy industries.

IN CONCLUSION

Over the course of this Cooperative Agreement, including a Management and Reporting Task, WRI proposed fifty eight tasks. Because of funding needs elsewhere in the Program, with DOE consent, Tasks 1.4 and 1.L were abandoned and never started. All the tasks proposed were successfully completed. WRI invested the research funds allocated for the Base Program in the development of energy production and environmental remediation technologies. Among the tasks funded, sixteen tasks either directly or indirectly involved WRI patented/licensable technologies. Several tasks that began under the Base Program eventually became successful JSR projects.

For the most part, the WRI Base Program supported the development of energy and environment-related technologies consistent with DOE priorities. Individual tasks addressed the needs of coal, oil and gas, and biomass-based energy systems.

As envisioned during the establishment of the Base Program, the Cooperative Agreement funded high-risk research in areas based on several factors:

- Our Nation's need for cheap electricity underscored the need to research, develop and demonstrate technologies for cleaning the stacks of existing coal-burning power plants.
- Our Nation's need for cheap electricity in the carbon constrained future, underscored the need for research, development and demonstration of enabling technologies toward zero emissions power plants of the future.
- Our Nation's appetite for transportation fuels and our desire to maintain our way and quality of life underscored the need for research, development and demonstration of technologies for the production of clean-burning liquid fuels.
- Our Nation's desire for energy independence underscored the need for technologies to upgrade and convert North American resources, unconventional resources such as oil shale.
- Our Nation's desire to curtail and reduce carbon emissions means cost-effective, sustainable renewable resources need to be integrated in our future energy mix. Technologies that co-develop renewable options within the fossil systems are likely to be more cost effective and efficient than stand-alone.
- Wyoming is the Btu capital of the Nation. There is a need for research activities dedicated to developing value-added energy products and associated economic benefits for the state and the region.

Under the Cooperative Agreement, WRI is responding to the energy research needs of our Nation and the region. The program has contributed significant benefits over the years for industry.

- Under the Cooperative Agreement, WRI has built a modular, well-instrumented coal combustion test facility that mimics a coal-fired utility boiler in residence time and furnace temperature profile. This facility is being used for technology development and technology verification projects for national and international utilities, for coal technology companies, and for combustion and emissions control equipment manufacturers.

    - working with our clients, we are testing new and cheaper methods for reducing NOx emissions such as injection of coal and biomass-based slurries, injection of hydrogen and syngas, injection of ozone;

- working with our clients, we are testing cheaper sorbents and methods for capturing mercury. One such scheme reinjects the unburnt carbon recovered from the fireball of the boiler to capture mercury. This technology, thief carbon, can reduce the cost of mercury capture to a fraction of that for conventional activated carbon. Thanks to our cooperative agreement with the USDOE, the thief carbon WRI made in the CTF was recently injected by a utility in a 600MW unit to show that indeed thief carbon is nearly as effective as activated carbon;
- working with our clients we are testing advanced combustion concepts such as oxy-fuel combustion as a multi-pollutant control strategy for not only the sequestration-ready, power plants of the future but developing a technology that can benefit our existing fleet of power plants; and
- working with our clients, we are looking to the future and testing cheaper ways of making oxygen. Novel concepts for separating oxygen from air for use in the coal combustion processes are being tested at the combustion test facility.

- WRI has been developing synthesis technologies to produce transportation fuels. One such technology can convert any carbonaceous feedstock into a mixture of alcohols, and the mixture is ready for use as a gasoline blend.

  - Imagine a confined animal feedlot. Animal waste is collected and processed in bio-digesters. Using the technology being demonstrated by WRI and partners, the digester gas becomes a mixture of alcohols for use in our cars, a transportation fuel.
  - Imagine a remote abandoned natural gas field. Using the technology being demonstrated, this field can make transportation fuel that can be trucked to the markets.
  - Imagine a biorefinery where forestry waste, animal waste, agricultural waste is processed using the technology developed at WRI to convert these renewable feedstocks into transportation fuel.
  - Imagine a power plant where Wyoming coal is the feed. Using the technology developed at WRI under the Cooperative Agreement, the plant not only produces electricity but also synthesizes mixture of alcohols.

  In conjunction with the appropriate gasification scheme this synthesis technology is a coal-to-liquids technology. In the same spirit, for remote natural gas fields this technology is a gas-to-liquid technology. As a biogas-based system, this technology is a means of capturing and converting green house gasses into a useful product.

- Under the auspices of the Cooperative Agreement, WRI is developing and testing unique, low-cost biomass gasification technologies for smaller-scale, distributed power generation applications. At WRI, we believe that our Nation's farmers and renewable energy are an essential part of our energy future. Technologies for distributed power

generation and distributed production of synthetic fuels and chemicals from renewable resources have been an integral part of research under the Cooperative Agreement.

- Under the auspices of the Cooperative Agreement, WRI has developed and patented a process for upgrading PRB coal by thermally removing mercury prior to combustion at the power plant, thus eliminating the need for costly carbon injection to meet new mercury regulations. A recent economic study for the Electric Power Research Institute has shown this process to be one of the lowest-cost technologies for removing mercury from PRB coal-fired power plants.

- Under the auspices of the Cooperative Agreement, WRI has developed a patented Thermal Enhancement (WRITE) process for heavy oil upgrading. The process a variant of the TaBoRR technology developed under the Base Program, converts bitumen (e.g. heavy oil, oil sands) into residuum-free oil whose density and viscosity meet pipeline specifications. A Canadian company has acquired the rights to the WRITE technology and is cosponsoring the development of a commercial-scale demonstration plant. When deployed, the technology will reduce our dependence on oil shipments from unstable parts of the world.

- In Wyoming, CBM produced water-related environmental issues are paramount in developing this resource. Under the Cooperative Agreement, WRI worked with producers to demonstrate beneficial agricultural and related uses for this precious water. At the same time, under the Base Program several new concepts were tested for water purification and reuse.

- WRI has taken a lead role in policy support for air quality regulations by creating and facilitating the Subbituminous Energy Coalition (SEC). The organization's approximately 50 members represent the major coal companies in the Powder River Basin, utilities burning PRB coal, railroads serving the PRB, and other interested parties. The SEC provides a forum for industry discussions on environmental control issues and provides a collective voice for PRB coal producers and users. The SEC has orchestrated a detailed review of proposed EPA mercury rules to ensure that subbituminous coal remains an environmentally acceptable and competitive fuel source. Looking to the future, SEC is poised to tackle CO_2 emissions and related issues.

- Under the Cooperative Agreement, WRI has developed value-added uses for power plant coal combustion by-products. Use of these materials for applications such as mine-site subsidence control, soil amendment, acid mine drainage mitigation, and construction were developed and tested.

- Environmental consequences of energy and fuels production are paramount in our research programs. Under the auspices of the Cooperative Agreement, WRI scientists developed and tested site-specific bio-remediation technologies for restoring contaminated soils and water.

- WRI has developed or made significant contributions to several environmental testing and sampling instruments currently (or soon to be) commercially available. Examples include Soil Test Kit for in-the-field quantitative analysis of hydrocarbon contaminants in soil, integrated storing field soil samples for volatile analysis, and the X-Wand, an instrument for measuring halogenated volatile organic compounds, a common but difficult to measure class of contaminants. All three are commercially available.

Looking to the future, WRI is continuing to implement an ambitious research and technology demonstration agenda under the new five-year Cooperative Agreement. With the establishment of the state-supported University of Wyoming School of Energy Resources, there is an opportunity for collaborative research between the University faculty and WRI staff. Collaborative research will also allow us to add an education and training component to our Cooperative Agreement projects thereby meeting our demand for trained energy professionals.